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Chemistry of graphene oxide. Reactions with transition metal cations

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ABSTRACT

The main advantage of graphene oxide (GO) over its non-oxidized counterpart, is its ability to form stable solutions, due to exfoliation to single-atomic-layer sheets. At present day, the fine chemical structure of GO remains ambiguous, while the traditional characterization methods have exhausted their potentials in revealing GO chemistry. Here we employ the NMR relaxation method to monitor reactions between GO and the three transition metal cations Mn^{2+}, Gd^{3+} and Fe^{3+} while in solution phase. We demonstrate that interaction between GO and metal cations is chemical in its nature. The GO functional groups serve as ligands replacing water molecules from the metal cations' first coordination sphere. The functional groups interacting at different pH values have been identified and quantified. At least part of the functional groups interacting with metal cations in neutral and basic solutions are alcohols that have acidic character. The metal ion induced rearrangement of the oxygen functional groups on GO platform points at the highly dynamic nature of GO, confirming the main standing points of our earlier proposed Dynamic Structural Model. For Fe^{3+}, the polynuclear complexes with hydroxide ion bridges form on the surface of GO; the process of the seeding the nanoparticles on GO surface is recorded.

1. Introduction

Graphene oxide (GO) became one of the most intensively studied materials of the last decade, being successfully tested for numerous applications. In particular, nanocomposites of GO with several metals found being promising in energy storage, fuel cells and catalysis [1]. These composite materials consist of nanometer-scale particles of metals and/or metal oxides anchored to GO sheets. Despite numerous papers reporting formation and use of such nanocomposites, the mechanism of their formation remains elusive. It is not even clear if any interaction between GO and metal cations takes place prior to the nanoparticle grow. Understanding of these interactions, from one side, would help to control the process, and subsequently the parameters of as-grown nanoparticles. From another side, this would shed additional light on GO chemistry that remains ambiguous despite intensive research.

The classical way of learning about chemical structure of any new substance is studying how it behaves being subjected to certain chemical reactions. Thus, thorough investigation of chemical reactions, their correct interpretation would help in understanding the actual chemical structure of GO. Since the pioneering work by Lerf et al. [2], up to the present day, substantial body of the studies on GO chemical properties were focused on attempts of covalent functionalization of GO [3–6]. Despite the large number of publications claiming such functionalization, solid and unambiguous demonstration of covalent bonding between GO and reacting species is very difficult [6]. First of all, different functional groups on GO platform cross-influence each other, changing the chemical behavior from that described in classical organic chemistry textbooks. Secondly, even if such functionalization takes place, it is difficult to confirm. Strictly, formation of covalent bonds can be demonstrated only spectroscopically by elimination of original GO bands and rise of the new ones. With multifunctional GO this is very difficult [6], especially by the commonly used methods that analyze solid GO samples.

One of the main advantages of GO, making it different from its non-oxidized counterpart and other 2D materials, is its ability to form stable solutions, by exfoliating to single-atomic-layer sheets. Thus, a successful chemical reaction involving GO should be conducted in solution phase to provide easy and unimpeded access to GO surface. To investigate such reactions, one needs the instrumental techniques applicable to solutions. Note, today most of the traditional instrumental methods, used for GO characterization (^{13}C SSNMR, FTIR, TGA, Raman etc.), investigate the solid material; they miss a crucial information about the chemistry of GO in solution. In our opinion, traditional spectroscopic methods, broadly used for

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